Charge Conjugation and Pairing in a model Cu_5O_4 Cluster

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Highly-symmetric three-band Hubbard Cu-O clusters have peculiar properties when the hole number is such that they admit W=0 hole pairs. These are two-hole eigenstates of the on-site Hubbard repulsion with eigenvalue 0, get bound by correlation effects when dressed by the interaction with the background, and cause superconducting flux quantization. We study the Cu_5O_4 cluster by exact diagonalization and show that bound electron pairs of $^1B_2$ symmetry are obtained at an appropriate filling, and quantize flux like the hole pairs. The basic mechanism for pairing in this model is the second-order exchange diagram, and an approximate charge conjugation symmetry holds between electron and hole pairs. Further, the flux quantization property requires that the W=0 pairs of d symmetry have s symmetry couterparts, still with W=0; the former are due to a spin fluctuation, while the latter arise from a charge fluctuation mechanism. The simultaneous existence of both is an essential property of our model and is required for any model of superconducting d pairs.

I. INTRODUCTION

Increasing experimental evidence obtained in several cuprate superconductors has convincingly demonstrated that the pairing state of these materials has $d-wave$ symmetry [1] and that the pairs exist above the critical temperature either in the form of superconducting fluctuations or preformed pairs. The latter aspect is apparent in the underdoped (normal) region in which a clear pseudogap essentially of the same magnitude as the superconducting gap is measured [2]. All these signatures put strict constraints to any microscopic model of the cuprates. Any theory of the paired state must predict the correct symmetry and doping dependence of the binding energy of the pair, but the pairing mechanism must be doping-independent and robust enough to survive superconducting fluctuations well into the normal state, far from optimum doping.

In BCS theory, the first-order repulsion between like charges is overcome by the second order interaction with phonons. In high-T_C superconductors the electron-phonon interaction is strong and phonons must be expected to contribute in an important way to the pairing interaction, although their task looks harder because the repulsion integral U is large (several eV). However, the straightforward idea that the hight-T_c phenomena are just a rescaled version of BCS theory is not granted. The role of phonons may be important, but is different, and some other ingredient is essential. First, due to the planar C_{4v} symmetry of these materials there is actually no repulsion barrier to overcome. In a series of papers [3–5] we have introduced the two-hole $^1B_2$ eigenstates with zero Coulomb on-site repulsion (the so called W=0 eigenstates). This is based on a standard two-dimensional Hubbard description of the particle correlations in the copper-oxide plane. The model has been numerically implemented in real space on highly symmetric Cu-O clusters containing up to 21 atoms and there the W=0 pairs arise from degenerate (x,y) levels. We have shown that when the first order interaction vanishes the net effect of the interaction is attractive in the physical parameter range. We used the smallest hole number (n=4 holes) necessary to form the W=0 pair on the degenerate $e(x,y)$ one-hole level of the clusters. Also, we have shown that although U is not small the dressing of W=0 pairs is perturbative; by exact diagonalization and diagrammatic analysis we demonstrated that the model leads to pair attraction of the order of tens of meV arising from virtual spin-flip excitations. Thus, rather than proposing a model of pairing, we have pointed out that the most standard description of electron correlations in the Cu-O plane already leads to pairing in clusters when the symmmetry of the problem is fully allowed. Remarkably, the off-site repulsive interactions, when included, tend to enhance the effect somewhat [4], so we devote the present study to the on-site interaction effects for simplicity. The mechanism we are considering is only a part of the story, but it seems to be the most peculiar part, being related to nothing but the C_{4v} symmetry. As such, the mechanism itself is doping-independent (although its effects do depend on doping). For similar reasons here we wish to make abstraction from phonon effects to see how far the simplified mechanism can account for reality by itself. We believe that a mechanism which predictably gets attraction out of repulsion is by itself of theoretical interest. Superconductivity is a much more complex problem than pairing, and the thermodynamic limit of the present model is currently under consideration; however, we pointed out [5] that the magnetic flux is quantized by our pairs in the same way as it is in the type II superconductors.

In the present paper we extend the analysis of Ref. [5] by diagonalizing the Cu_5O_4 cluster with increasing number n of holes. Eventually, we find electron pairing, again with a binding energy Δ(n) of a few tenth of eV in the physical parameter space. Electron pairing is actually realized [6], e.g., in the T' structure of $(Nd,Ce)_2CuO_4$ exhibiting superconductivity. The T' structure of this compound is different from the T structure of La_2CuO_4, but is still characterized by CuO_2 planes [7].Our main point here is that electron pairs and hole pairs are related by an approximate charge conjugation symmetry and the very same basic mechanism or diagram is operating in both cases. Further, we demonstrate how the two different symmetries (A_1 and B_2) of W=0 singlet pairs allowed by our theory produce the superconducting flux quantization phenomenon, both for electron and hole pairs, in the respective doping regimes, and are thus both necessary for a serious proposal of a mechanism of pairing.

II. CHARGE CONJUGATION

By a canonical transformation from holes to electrons, the three-band Hubbard Hamiltonian we considered previously [3] becomes:

$$H=\sum_i(2\varepsilon_i+U_i)-\sum_{i\sigma}(\varepsilon_i+U_i)a^+_{i\sigma}a_{i\sigma} - \sum_{<i,j>\sigma}t_{ij}a^+_{i\sigma}a_{j\sigma}+\sum_i U_i n_{i+}n_{i-}, \qquad (1)$$

with $a^+_{i\sigma}=c_{i\sigma}$ and $a_{i\sigma}=c^+_{i\sigma}$ creating or destructing an electron of spin $\sigma=\uparrow,\downarrow$ at site i, respectively. Thus, in the electron representation the signs of the site and hopping integrals are reversed. The single-electron energy levels of the Cu_5O_4 cluster have been computed in the physical range of parameters (in eV) used before, *i.e.*, U_d=5.3,U_p= 6, t=1.3,ε_d=0,ε_p=3.5 and the results are displayed in Fig.1 as a function of the oxygen-oxygen hopping integral t_{ox}. With respect to the hole case [3], the sequence of levels is such that bonding and antibonding states are interchanged. According to symmetry arguments [4], singlet pair eigenstates of the Hamiltonian

H with zero eigenvalue of the interaction part and $^1B_2$ symmetry exist when two particles sit on a degenerate $e(x,y)$ level. In the hole representation the antibonding state of e symmetry contains two holes when 14 holes are present in the cluster. Its charge-conjugate counterpart (since the dimensionality of the one-body basis is 18) corresponds to a total of 4 electrons in the cluster, two of them filling the lowest a_1 bonding state and the other two sitting on the next $e(x,y)$ level of Fig.1.

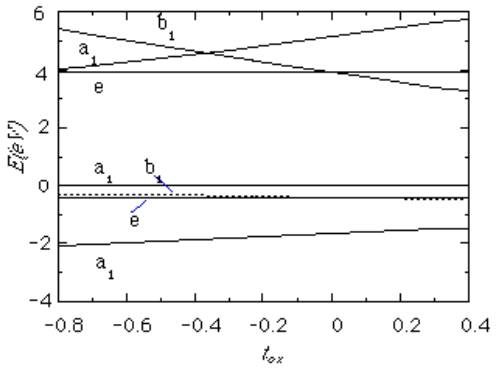

FIG. 1. One-electron energy levels of the Cu_5O_4 cluster versus t_{ox}. Parameters are given in the text. The levels are labelled according to the representations of the C_{4v} Group.

In the symmetric Cu_5O_4 cluster we previously found [3] that the exact diagonalization of the Hamiltonian matrix with four holes in a wide range of negative t_{ox} values for the $^1B_2$ singlet gives a negative pairing energy $\Delta(4)$, where Δ(n) =E(n)+E(n-2)-2 E(n-1), and E(n) is the ground state energy with n holes. Therefore one expects that $\Delta(14)$ is negative while $\Delta(12)$, which corresponds to the complete filling of the upper e(x,y) level with $^1A_1$symmetry, is highly repulsive. Typical energies Δ computed with t_{ox}=- 0.2 eV and different hole numbers are listed in Table 1.

The t_{ox} dependence of Δ computed using an enhanced Lanczos diagonalization routine is shown in Fig.2 and Fig.3 for $\Delta(4)$ and $\Delta(14)$ and for $\Delta(10)$ and $\Delta(12)$, respectively. Filling the levels with n holes, pairing occurs when the uppermost pair is a W=0 singlet. It is apparent that a considerable degree of symmetry under e-h exchange exists in the cluster and that the pairing interaction is not restricted to a single value of doping. The electron-hole symmetry is not exact, because the one-electron energy level spectrum of Fig. 1 is not invariant when up is exchanged with down and left with right ($t_{ox} \rightarrow -t_{ox}$ and $E \rightarrow -E$); however one could have predicted the negative Δ and its magnitude by the approximate symmetry. In real systems electron superconductivity has been first reported [6] in the Nd_2CuO_4 doped with Ce with a maximum T_c=24 K for optimal doping concentration x=0.15, similarly to more common hole superconductors. $Nd_{2-x}Ce_xCuO_4$ is an example of high-T_c cuprate in which charged carriers are electrons.

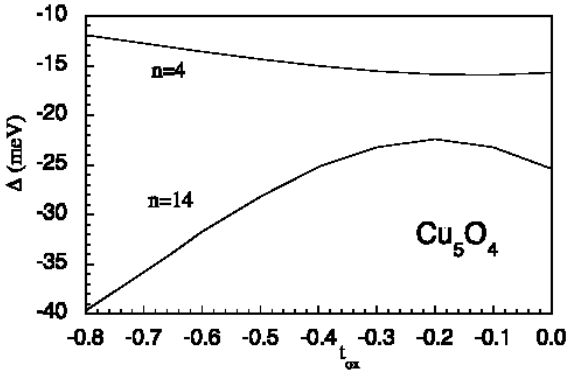

FIG. 2. Pairing energy Δ(n)=E(n)+E(n-2)-2 E(n-1) of the Cu_5O_4 cluster with n=4 and n=14 holes.

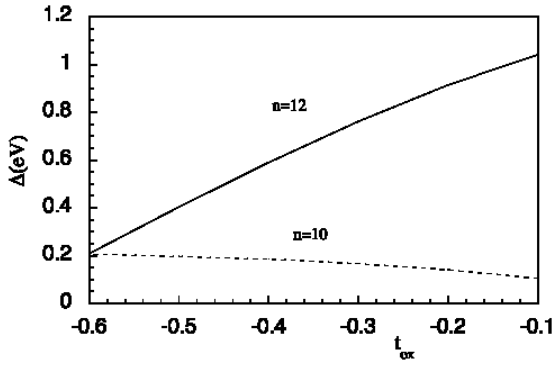

FIG. 3. $\Delta(n)$ as a function of t_{ox} for n=10 and n=12.

The spin-flip diagram responsible for the pairing has been identified before [5]. The shift of the pair energy was found, after considerable algebra, in terms of the one-body site amplitudes. When $\Delta(4)$ is computed, the background holes are just 2, and occupy an orbital of a_1 symmetry, which we denote by a. Empty states (antibonding and nonbonding) of the same symmetry will be denoted by a', and we shall write b for the empty states of b_1 symmetry. To second-order one obtains for Δ the following expression:

$$\Delta = -2\left[\sum_b \frac{W(a,b,x,x)^2}{(\epsilon_b - \epsilon_a)} - \sum_{a'} \frac{W(a,a',x,x)^2}{(\epsilon_{a'} - \epsilon_a)}\right] \quad (2)$$

where $W(k,l,m,n) = \langle k_+ l_- | \sum_i U_i n_{i+} n_{i-} | m_+ n_- \rangle$ and the sums run only over the one-body states of a and b symmetry since the contribution of the $e(x,y)$ orbitals vanishes. The final sign of Δ is determined by the relative weight of the virtual excitations to the empty states of different point symmetry.

It is important to check the range of validity of the perturbative expansion by comparing the results of Eq.2 with the exact diagonalization values of Δ. We construct the normalized hole states of symmetry $a, b, e(x, y)$ whose site amplitude and energy are listed in Table II. Making use of the above standard values of the parameters we calculate the accuracy $\delta = 2\left|\frac{\Delta_{ex}-\Delta_{appr}}{\Delta_{ex}+\Delta_{appr}}\right|$ for n=4 as a function of negative t_{ox}'s, i.e. in the region of pairing. The accuracy is good (about 3%) for small U values ($\leq$ 0.05 t) and raises steeply to approximately 30% for larger values of U/t with a smooth dependence on t_{ox}. However, for t_{ox}=0 where the pairing is strongest for the $^1B_2$ singlet, the accuracy is around 7% up to U/t $\approx$1.

The values $U_d = 5.3$ eV, $U_p = 6.$ eV differ appreciably from other literature estimates [8], and must depend on the compound and doping. For La_2CuO_4, U_p=4 eV and U_d=10.5 eV have been recommended [9]. None of the above results depends qualitatively on the precise value of the model parameters, since ours is basically a symmetry argument.

III. FLUX QUANTIZATION AND PAIR SYMMETRY

Consider the ground-state energy E(ϕ) of a two- dimensional system as a function of the magnetic flux ϕ through it. This is definitely a most compelling way of testing its superconductivity, since type II superconductors quantize the flux for integer and half-integer multiples of $\phi = \frac{hc}{e}$. If one inserts a flux tube in a loop formed by closing the path on the external Cu of the Cu_5O_4 cluster, one finds [5] that the calculated ground state energy E(4) has a second minimum at $\phi_0/2$ well separated from a barrier from the ϕ=0 minimum. The point symmetry of the wavefunction changes from$^1B_2(x^2 - y^2)$ at ϕ=0 to $^1A_1(x^2 + y^2)$ at ϕ=$\phi_0/2$. Owing to the symmetry under charge conjugation and to the attractive interaction of the E(14) state, one expects to find the specular situation in the electron case. That this is indeed the case it is apparent from Fig.4 where the response functions R=[E(ϕ)-E(0)]/t_d of the hole- and electron-doped cluster are compared. Here t_d is an (in principle, infinitesimal) hopping energy between the external Cu's, which is needed to close the loop around the tube. Due to the small size of the system the barrier preventing the condensation of pairs is finite but of comparable height in both cases. The symmetry of the states is the same as in the hole case, i.e., $^1B_2$ for ϕ=0 and $^1A_1$ for ϕ=$\phi_0/2$.

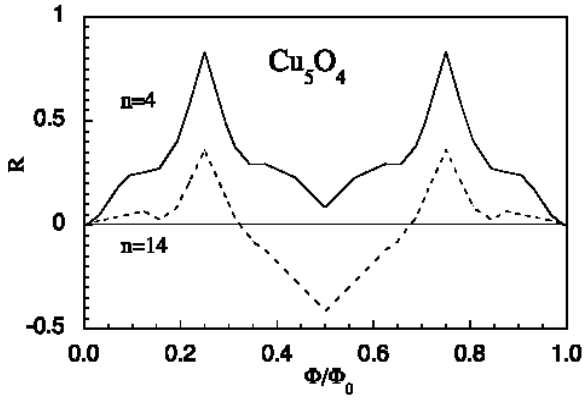

FIG. 4. Response function R versus the normalized flux for the Cu_5O_4 cluster with n=4 and n=14 holes.

However, the mechanism of interaction between the holes (electrons) is basically different for $^1B_2$ and $^1A_1$ W=0 pairs. Consider again the interesting case t_{ox}=0 for which all the oxygens are equivalent and the point symmetry Group is S_4. Within the space of B_2 symmetry spanned by the |xy> and |yx> two-body states the contribution to the scattering amplitude is zero to first-order, but finite and negative to second order. Thus the anomalous propagator $A_{sf} \approx \frac{i\Delta^{(2)}}{(\omega-2\epsilon)^2}$ scatters the $|y_+x_- >$ state out of the $|x_+y_- >$ state where $\Delta^{(2)}$ is given in Eq.2 and ϵ is the energy of the unperturbed $e(x, y)$ states. The interaction is attractive for the lowest state of $^1B_2$ symmetry and involves a second order spin-flip fluctuation.

Consider now the basis of the degenerate |xx>+| yy> states and the |bb> states all having $^1A_1$ symmetry. The eigenvalue problem requires the diagonalization of the 2×2 matrix:

$$\begin{vmatrix} < bb|W|bb > & < bb|W|x^2+y^2 > \\ < bb|W|x^2+y^2 > & < x^2+y^2|W|x^2+y^2 > \end{vmatrix} = \begin{vmatrix} \frac{U_p}{4} & \frac{U_p}{2\sqrt{2}} \\ \frac{U_p}{2\sqrt{2}} & \frac{U_p}{2} \end{vmatrix} \quad (3)$$

where U_p is the on-site repulsion at the oxygen site. The lowest eigenvalue is 0 and the W=0 pair is $\psi = -\sqrt{\frac{2}{3}}|bb\rangle + \sqrt{\frac{1}{3}}|x^2+y^2 >$. The upper eigenvalue is 3U/4 and the eigenfunction $\psi = \sqrt{\frac{1}{3}}|bb\rangle + \sqrt{\frac{2}{3}}|x^2+y^2 >$. Thus we have a first-order mechanism involving a *charge* fluctuation.

By looking at Fig.4 we realize that with increasing the flux ϕ, the $^1B_2$ component of the ground state is quickly destabilized by the vector potential, while the $^1A_1$ component decreases in energy and eventually becomes energetically favored in presence of the trapped flux. A similar change of symmetry occurs in conventional superconductors where the Cooper wavefunction has *s* symmetry

[10]. The Hubbard large U system is stabilized by the intrinsic charge fluctuation. Since the mechanism is robust (first order) it is conceivable that these low lying pairing states can survive in the vortex core of the underdoped phase [2]. The $^1A_1$ symmetry of the ground state in the presence of the half flux quantum is required by general symmetry principles. Indeed, the vector potential lowers the symmetry from C_{4v} to its abelian subgroup Z_4, which contains only the rotations. In Z_4,$^1B_1$ and $^1B_2$merge into the same irreducibe representation and so the vector potential mixes them, giving rise to W$\neq$ 0 pairs. This does not apply to the $^1A_1$ state, which remains single and W=0. With increasing the flux, the W$\neq$ 0 component of the ground state increases its energy, until it crosses the $^1A_1$ pair energy. The minimum at half flux quantum corresponds again to a Δ <0 situation. It is gratifying that the present model allows for W=0 pairs of both symmetries, because this is the only way the superconducting flux quantization works.

IV. CONCLUSIONS

We have investigated the symmetry properties of the W=0 pairs under charge conjugation by performing numerical diagonalizations of the Cu_5O_4 cluster doped with a variable number of holes n ranging from 0 to 14. We find attractive interaction of comparable strength whenever the bonding and antibonding degenerate levels of $x-y$ symmetry are half-filled. All the other fillings lead to strong repulsion. The 14-hole case corresponds to the doping with 4 electrons and thus to electron superconductivity. In all cases the attraction is provided by the spin-flip fluctuation between $|x_+y_- >$ and $|y_+x_- >$ pairs. The n=4 and 14 hole $^1B_2$ states quantize the superconducting flux and the ground states in presence of zero and one fluxon have different symmetry as in BCS superconductors.

V. ACKNOWLEDGMENTS

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TABLE CAPTIONS

TABLE I. Δ values of the Cu_5O_4 cluster vs the number of holes n computed with the standard set of parameters given in the text and t_{ox}=-0.2 eV.

TABLE II. Symmetry, site amplitude and energy of one-hole levels for the Cu_5O_4 cluster. In the first row we report the Cartesian coordinate of each site in units of the Cu-O distance. The first column shows the orbitals; a_0 is the nonbonding level belonging to the Irrep A_1. Minus and plus superscripts refer to bonding and antibonding levels, respectively.

TABLE I

n holes	Δ(meV)
4	-15.9
10	141.2
12	914.7
14	-22.4

TABLE II

	(0,0)	(1,0)	(0,1)	(-1,0)	(0,-1)	(0,-2)	(2,0)	(0,2)	(-2,0)	energy
a	2γ	$\frac{\epsilon\gamma}{2t}$	$\frac{\epsilon\gamma}{2t}$	$\frac{\epsilon\gamma}{2t}$	$\frac{\epsilon\gamma}{2t}$	$\frac{\gamma}{2}$	$\frac{\gamma}{2}$	$\frac{\gamma}{2}$	$\frac{\gamma}{2}$	$\epsilon_a^{\pm} = \frac{1}{2}\left\{\epsilon_p + 2t_{ox} \pm [(\epsilon_p + 2t_{ox})^2 + 20t^2]^{\frac{1}{2}}\right\}$
x	0	$\frac{\alpha}{\sqrt{2}}$	0	$-\frac{\alpha}{\sqrt{2}}$	0	0	$\frac{\beta}{\sqrt{2}}$	0	$-\frac{\beta}{\sqrt{2}}$	$\epsilon_x^{\pm} = \frac{1}{2}\left\{\epsilon_p \pm [(\epsilon_p^2 + 4t^2)]^{\frac{1}{2}}\right\}$
y	0	0	$\frac{\alpha}{\sqrt{2}}$	0	$-\frac{\alpha}{\sqrt{2}}$	$-\frac{\beta}{\sqrt{2}}$	0	$-\frac{\beta}{\sqrt{2}}$	0	$\epsilon_x^{\pm}$
b	0	$\frac{\alpha_1}{2}$	$-\frac{\alpha_1}{2}$	$\frac{\alpha_1}{2}$	$-\frac{\alpha_1}{2}$	$\frac{\beta_1}{2}$	$-\frac{\beta_1}{2}$	$\frac{\beta_1}{2}$	$-\frac{\beta_1}{2}$	$\epsilon_b^{\pm} = \frac{1}{2}\left\{\epsilon_p - 2t_{ox} \pm [(\epsilon_p - 2t_{ox})^2 + 4t^2]^{\frac{1}{2}}\right\}$
a_0	$\frac{1}{\sqrt{5}}$	0	0	0	0	$-\frac{1}{\sqrt{5}}$	$-\frac{1}{\sqrt{5}}$	$-\frac{1}{\sqrt{5}}$	$-\frac{1}{\sqrt{5}}$	0

$\alpha = \frac{t}{\sqrt{t^2+(\epsilon_x^{\pm}-\epsilon_p)^2}}; \alpha_1 = \frac{t}{\sqrt{t^2+(\epsilon_b^{\pm}+2t_{ox}-\epsilon_p)^2}}; \beta = \frac{\alpha}{t}(\epsilon_x^{\pm} - \epsilon_p); \beta_1 = \frac{\alpha}{t}(\epsilon_p - \epsilon_b^{\pm} - 2t_{ox});$
$\gamma = \frac{t}{\sqrt{(\epsilon_a^{\pm})^2+5t^2}}$